Magnetite Oxidation: A Proposed Mechanism

Abstract. *All magnetites are oxidized topotactically with formation of solid solution at temperatures below 400°C. The oxidation of hematite-free magnetites proceeds to* γFe_2O_3*, whereas in the presence of hematite epitaxial growth of* αFe_2O_3 *takes place, with excess iron ions being returned to the solid solution. A method for synthesizing maghemite from natural magnetites is indicated.*

The oxidation of magnetites at high temperatures (greater than 600°C) leads always to the formation of αFe_2O_3 (hematite). At lower temperatures, however, the oxidation of magnetites proceeds otherwise, depending on the origin and nature of the starting magnetite. Usually, synthetic precipitated magnetites, when oxidized below 400°C, give γFe_2O_3 through a topotactic (*1*) oxidation of the magnetite to a solid solution of γFe_2O_3 in Fe_3O_4. This oxidation is completed without alteration of the inverse spinel structure of the starting magnetite (*2*).

Natural magnetites, when oxidized between 200° and 500°C, are partially oxidized to an end product, in which the grains are constituted by a core of unoxidized magnetite covered by a protective layer of αFe_2O_3. This protective layer of αFe_2O_3 is obtained in the disproportionation of a previously formed solid solution (*3, 4*). Moreover, such disproportionation is catalyzed by αFe_2O_3 when this product has been formed in the oxidation of the same magnetite. Furthermore, the specific surface area of the magnetite, which others (*5*) assumed to be the controlling factor of the oxidation reaction, participates only in the kinetics of the oxidation.

Our new data, obtained with an x-ray Guinier diffraction camera, indicate that the magnetites oxidized at low temperature with the formation of both solid solution and αFe_2O_3 contain, initially, at least a trace of αFe_2O_3. On the other hand, those magnetites which in the low-temperature oxidation form γFe_2O_3 do not contain a detectable amount of αFe_2O_3 (0.005 percent being the limit of detection). These facts thus indicate the catalytic role of αFe_2O_3 in the first stage of oxidation of the magnetite.

To elucidate this catalytic role, mixtures of pure magnetites and of αFe_2O_3 were submitted to isothermal oxidations from 150° to 300°C in air at atmospheric pressure. The autocatalytic action of αFe_2O_3 occurs only if the mixtures of magnetites and αFe_2O_3 have been subjected, prior to the oxidation step, to pressures of at least 10^4 bar at room temperature. This effect increases after compression at higher pressures (2×10^4 bar), as indicated by the amount of αFe_2O_3 formed in the subsequent oxidation at atmospheric pressure. However, a complete conversion of the γFe_2O_3 to αFe_2O_3 was not achieved. In order to convert all of the solid solution (or the γFe_2O_3) into αFe_2O_3 at low temperatures (150° to 300°C), it was necessary (*4*) first to form a partially oxidized solid solution which is then converted to $\alpha Fe_2O_3 + Fe_3O_4$ by heating in an inert atmosphere to more than 600°C, and finally to submit this product to oxidation at low temperature.

Natural magnetites from Mineville, New York, and Malmberget, Sweden, were purified from αFe_2O_3 by heating in a controlled atmosphere ($CO:CO_2$, 1:30) at 1000°C for 60 hours (*6*). Magnetites so purified are hematite-free within the limit of experimental detection. These magnetites, which form a protective layer of αFe_2O_3 (*4*) as the final product of low-temperature oxidation, after purification are oxidized to γFe_2O_3 at temperatures between 200° and 300°C.

Thus there appears to be a single mechanism for the oxidation of all magnetites. The transformation of the magnetite during oxidation is a topotactic process (*1*) with formation of a solid solution by migration of iron ions toward the surface of the grains, where oxygen has been adsorbed and ionized. In the presence of αFe_2O_3, the solid solution may be converted epitaxially to αFe_2O_3 with the iron ions, in excess with respect to stoichiometric Fe_2O_3, flowing back into the residual solid solution which eventually is retransformed into magnetite.

In all cases at temperatures above 600°C the final oxidation product is 100 percent αFe_2O_3. At lower temperatures, the aforementioned mechanism allows two possibilities:

1) In the total absence of αFe_2O_3, the end product of the topotactic oxidation is γFe_2O_3.

2) In the presence of αFe_2O_3, both topotactic and epitaxial transformations proceed, the end product being determined essentially by kinetic conditions: if the kinetics of the topotactic transformation prevails, this reaction goes to the formation of γFe_2O_3 which is totally converted to αFe_2O_3 at the same low temperature. If the kinetics of the topotactic and epitaxial processes are competitive, then the topotactic transformation gives rise only to solid solution, and the reaction proceeds until a protective layer of αFe_2O_3 covers a core of magnetite. Factors affecting the kinetics of these low-temperature reactions are specific surface area, presence of lattice imperfections (such as vacancies), dislocations, or impurities.

A further result of our studies is that γFe_2O_3 (maghemite) has been synthesized in the laboratory from natural magnetites for the first time.

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References and Notes

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Disposable Hydrogen Generator

Abstract. *A convenient means of producing hydrogen gas for anaerobe jars or other situations where 2 liters of hydrogen will suffice is described. Hydrogen gas is produced by the chemical action of magnesium metal, zinc chloride, sodium chloride, and water within a unique plastic and aluminum foil envelope. That there is no excessive buildup of hydrogen greatly reduces the hazard of explosion. The gas-producing units are simple to activate and may be discarded after use.*

Cultivation of anaerobic bacteria requires an oxygen-free environment. For this purpose, physical systems incorporating gases often require cumbersome equipment. Biological systems are generally slow. Various chemical proc-

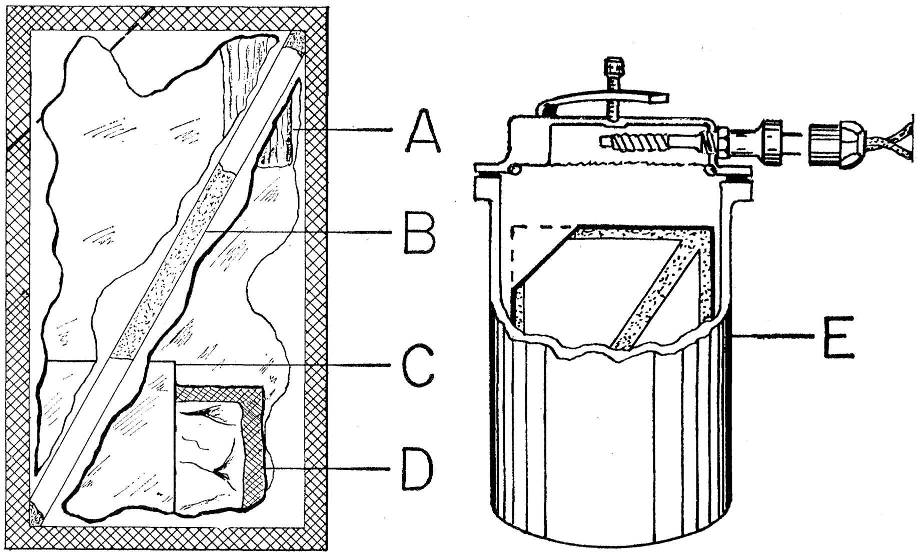

Fig. 1. (Left) A cutout view of the hydrogen generator. *A*, Coarse filter; *B*, heat seal; *C*, fine filter; *D*, absorbent paper bag containing chemicals. (Right) *E*, Position taken by generator in the anaerobe jar.

esses, such as conversion from sodium borohydride (*1*), have been used with moderate success; but expense and the special handling limit their application. We now describe a unit for the controlled generation of a determined volume of hydrogen gas sufficient to produce an effective anaerobic atmosphere within an anaerobe jar (*2*).

The unit is contained in a polyethylene, aluminum-laminated envelope of convenient size for use in the standard Brewer jar. The envelope is diagonally heat-sealed into two approximately equal compartments, and sandwiched between the seal are two pieces of filter paper as shown in Fig. 1. The lower compartment contains 5.0 g of finely divided magnesium granules, 2.5 g of sodium chloride, and 1.0 g of zinc chloride, the chemicals having been mixed in a ball mill. The mixture is sealed in an absorbent paper bag which provides for even water absorption by the contents. The overall reaction appears to proceed as follows:

$$Mg + ZnCl_2 + 2H_2O \xrightarrow{NaCl} MgCl_2 + Zn(OH)_2 + H_2$$

The reaction is initiated by cutting off the corner of the envelope and adding 10 ml of water. The water forms a pool in the upper compartment and flows slowly into the bottom compartment through an absorbent intracompartmental filter. The rate of flow may vary, and it depends on the absorbency of the paper used. Retardation of the flow serves two important functions. First, it delays the reaction for up to 60 seconds, the time required for the water to penetrate the absorbent paper, and the operator has time to cover the anaerobe jar before the reaction begins. Second, a controlled rate of flow from top to bottom compartment of the envelope is established. This is a function of penetration and is important in determining the rate of reaction and subsequent evolution of hydrogen gas. The reaction, therefore, proceeds at a controlled rate. The gas is exhausted at the cutoff corner of the envelope.

The volume of oxygen in the air contained in the jar is about 598.5 ml. A minimum of 1197 ml of hydrogen gas is required if all of the oxygen is to be consumed in the catalytic reaction. The volume of hydrogen gas produced in the first 35 minutes runs between 1400 and 1800 ml. At the end of 4 hours 2000 ml of gas is produced. All measurements were made by the water displacement technique. The platinum or palladium catalyst continues to function until all the oxygen is consumed. Owing to the chemical reaction, temperatures inside the jar range from 26°C to 30°C, thereby being suitable for immediate incubation of the cultures. This method of providing anaerobic conditions has been used in our laboratories and those of the Bacteriology Section of the Maryland State Health Department (*3*), for growing 15 species of *Clostridium*, including *Cl. novyi, Cl. botulinum, Cl. tetani, Cl. sporogenes, Cl. histolyticum*, and *Cl. perfringens*. Also, *Bacteroides fragilis, B. funduliformis, Fusobacterium fusiforme*, and a species of *Veillonella* have been isolated by this technique. Gas samples collected from the units were analyzed by gas chromatography. The only gas produced was hydrogen.

One of the advantages of the Brewer jar is that it does not need to be evacuated; thus the carbon dioxide in the atmosphere is not removed. Nor, owing to the acidic nature of the reaction, is any of the carbon dioxide present in the atmosphere absorbed. Other replacement techniques are recommended for organisms requiring as much as 10 percent carbon dioxide.

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Complement: Inactivation of Second Component by p-Hydroxymercuribenzoate

Abstract. p-*Hydroxymercuribenzoate inactivates the second component of complement whether it is in solution or is fixed to a sensitized erythrocyte together with the first and fourth components. Inactivation by the drug is blocked but not reversed by cysteine. Partial purification of the second component of complement is described.*

The possible role of sulfhydryl groups either in preserving the structural integrity of components of complement (C′1, C′2, etc.), or in the participation of these components in immune hemolysis, has been investigated with the reagent *p*-hydroxymercuribenzoate (PHMB). While this reagent had no significant effect on the activities of C′1, C′4, and the C′3 complex, it did inactivate the second component of complement, C′2, both in solution and when fixed to the cell in the complex EAC′1a,4,2 (*1*).

The C′2 for this investigation was obtained from human serum. The C′3 activity was removed from the serum by precipitation with 1 percent rivanol